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MASS SPECTROMETER STUDY OF METAL-CONTAINING FLAMES

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FIFTH QUARTERLY TECHNICAL SUMMARY REPORT
1 October - 31 December 1962

ARPA Order No. 23-62, Amendment 28
Project Code No. 9100

M.R.I. Project No. 2551-P

For

Director
Advanced Research Projects Agency
Washington, D. C.

(Contract No. Nonr-3599(00))

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MIDWEST RESEARCH INSTITUTE

⑥ MASS SPECTROMETER STUDY OF METAL-CONTAINING FLAMES

by

⑧ Thomas A. Milne

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SUMMARY

The one atmosphere molecular beam sampling system has been further characterized by studying beam intensities as a function of orifice-to-skimmer distance. Measurements on binary mixtures of gases reveal "mass-separation" effects larger than those previously reported. Enrichment of the heavier component occurred in the beam in all cases and amounted to as much as a 25-fold increase in the $Argon/H_2$ ratio for an equimolar H_2-Argon mixture. The species Cl, HCl and HBO_2 have been sampled from a one atmosphere H_2-O_2 stoichiometric flame to which about one per cent BCl_3 had been added.

I. INTRODUCTION

In the four preceding quarterly reports we have described the development of a molecular beam sampling system suitable for sampling one atmosphere sources and have described initial experiments with simple gases and the N_2O_4-NO_2 equilibrium. This sampling system, using rather modest pumps, achieves beam intensities of the order of 1×10^{17} molecules/cm^2/sec at the third or collimating slit and reflects ordered motion from the first orifice into the mass spectrometer.

In this report are described (1) additional experiments aimed at characterizing the process by which beams are formed from one atmosphere sources, (2) studies of "mass-separation" effects in sampling gaseous mixtures, (3) further work on the N_2O_4-NO_2 equilibrium, and (4) application of the sampling system to one atmosphere flames.

II. SAMPLING OF PERMANENT GASES AND MIXTURES AT ONE ATMOSPHERE

A. Simple Gases

There have been no basic changes in the sampling system as described in the last quarterly report. Rather we have kept the same general sizes and arrangements of slits but varied certain parameters, chiefly the orifice to skimmer distance. In our apparatus it is most convenient to move the orifice while leaving the skimmer and all other slits fixed. A simple permanent gas inlet system was used which consisted of a 1/2 in. stainless steel tube with an 0.005 in. thick disk, containing an 0.010 in. diameter orifice, soldered to one end. This tube was held and positioned by a simple Veeco quick-connect vacuum coupling which allowed it to be moved up and down relative to the skimmer. The whole quick-connect assembly could also be translated in any direction to allow alignment at each distance or to permit systematic beam misalignment.

The 0.010 in. diameter orifice size represents about the largest diameter that can be used at low temperature and one atmosphere with the available first stage pumping capacity. With flames, orifices of as large as 0.015 in. have been successfully used, due to the lower mass throughput of the hot gases. It is important to be able to obtain good molecular beams with large orifices to minimize the plugging problems associated with the metal additives in flame studies.

With this apparatus and with pure Argon, data were taken on beam and background signal strength as a function of orifice-to-skimmer distance at

various pressures. Figures 1, 2 and 3 show the behavior observed. The pressure ratio across the orifice is determined in these experiments by the size of the orifice, the nature of the gas and the pumping speed of the 7-in. oil diffusion pump at the operating pressure. As can be seen from data in Figs. 2 and 3, we are operating the pump very near its upper limit and its speed is not linear with P_o ; consequently, the expansion pressure ratio is not constant.

At the highest source pressure the beam signal drops off very rapidly with increasing orifice-to-skimmer distance. In fact, it becomes increasingly difficult to find any sharp maximum for the beam or total signal in the vicinity of the true optical alignment. However, one can find a second maximum in the beam intensity when the orifice is moved sufficiently far in any direction from true alignment. This behavior is shown in Figs. 4 and 5 for pure Argon at 693 Torr and for two orifice-to-skimmer distances. At 1/4 in., a good beam is obtained while at 3/8 in., the signal was only slightly shutter-dependent. P_2 , the second stage pressure (downstream of the skimmer) also rises to a maximum as the orifice is moved out from the center.

Further experimentation of this type should help define the nature of the expansive flow and its interaction with the skimmer. In particular, one may be able to establish those conditions under which the gas will pass through shocks as it converts into a molecular beam. For the moment, however, we can use this type of data simply to predict the optimum geometrical conditions for a good beam and to determine what factors are limiting the available beam intensity at one atmosphere. To help decide the latter, a scattering correction was applied to the beam data shown in Figs. 2 and 3. The dotted curves show the results. It turns out that only scattering in stage 2 is significant and this correction does little to improve the maximum beam intensity. Thus, it appears that increased pumping capacity in stages other than the first would serve mainly to further increase the ratio of beam to background. These scattering corrections do not explair the sharp drop in beam intensity as the orifice approaches the skimmer and this is probably caused by some aerodynamic interaction with the skimmer.

One other observation of interest is that a strongly oscillatory beam signal, but not background signal, was often observed at larger orifice-to-skimmer distances where the beam intensity was rapidly decreasing. This same oscillation was also observed at the position of the second maximum surrounding the central beam position. This may be an indication of the presence of a shock or other discontinuity in the flow.
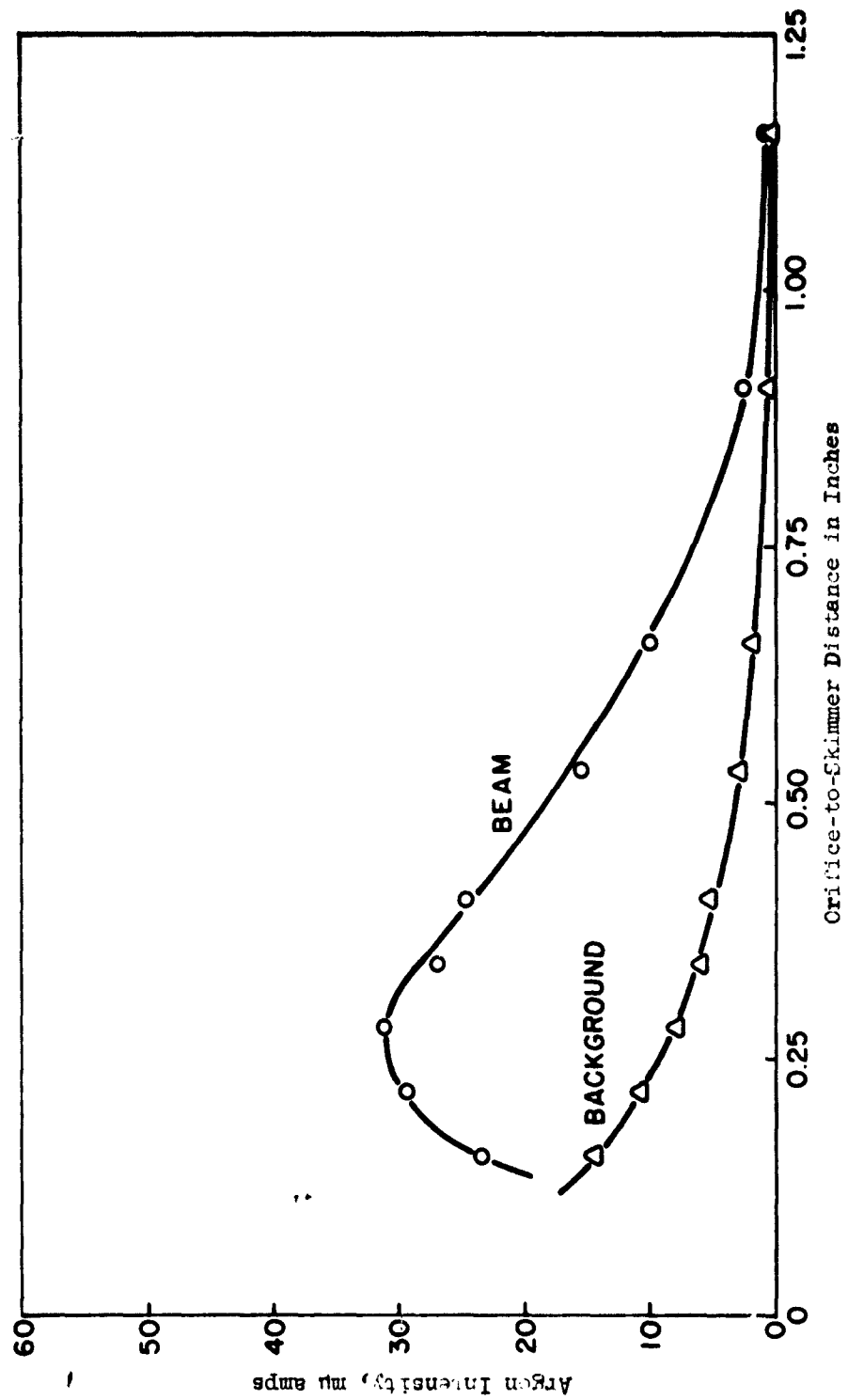
Fig. 1 - Variation of Beam Intensity With Orifice-to-Skimmer Distance
(Source Pressure = 96 Torr)

Fig. 2 - Variation of Beam Intensity With Orifice-to-Skimmer Distance
(Source Pressure = 400 Torr, P_1 = 13 microns)
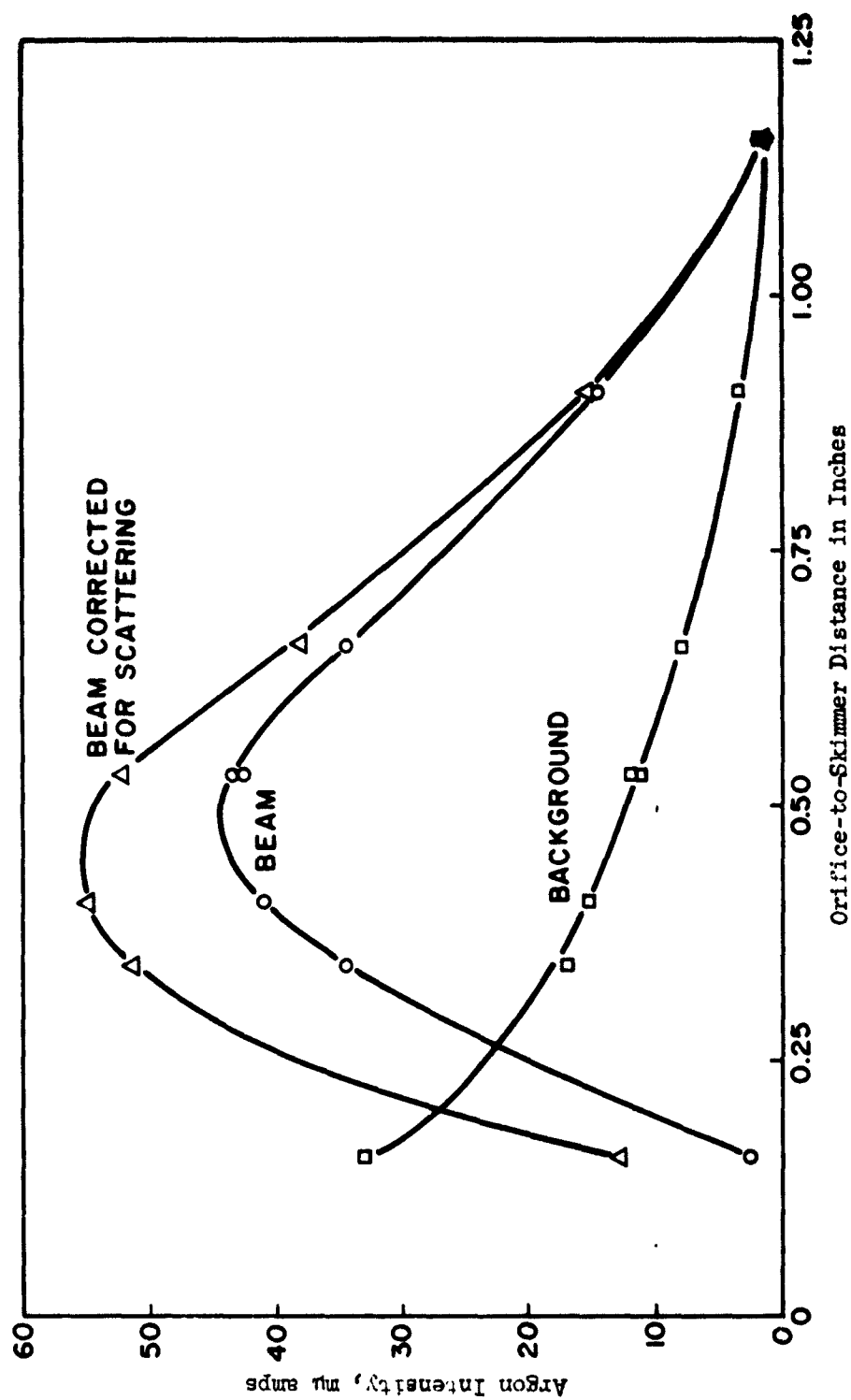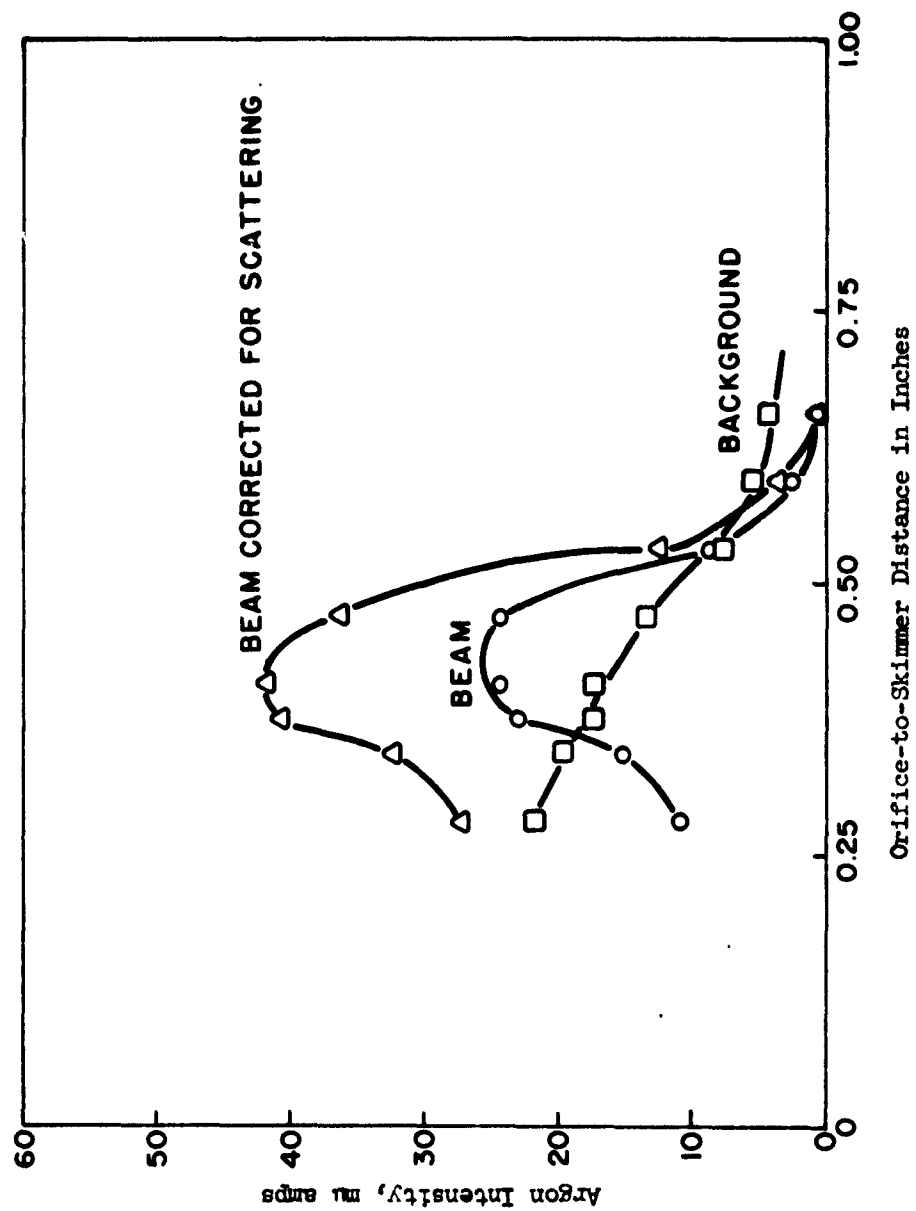
Fig. 3 - Variation of Beam Intensity With Orifice-to-Skimmer Distance
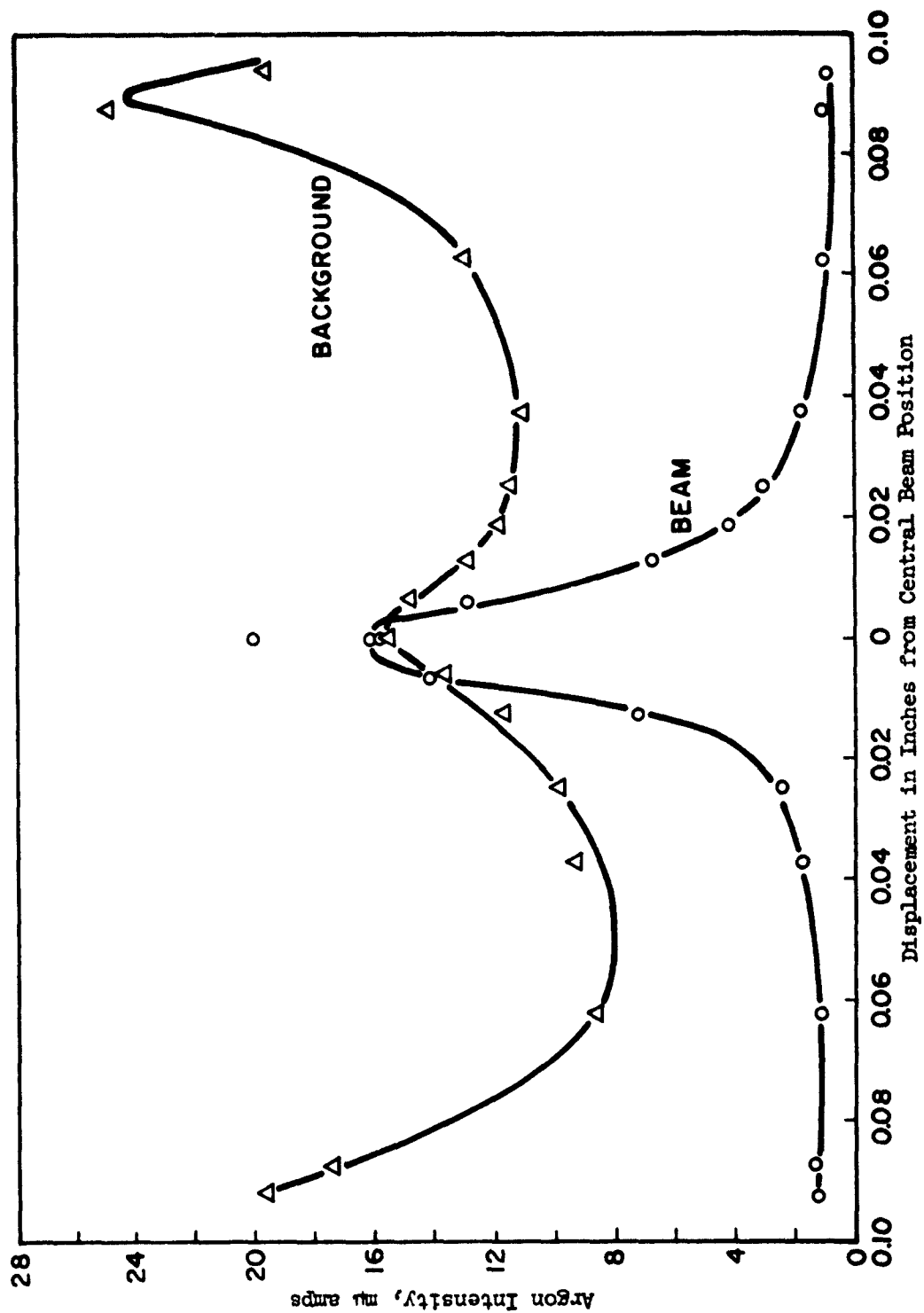(Source Pressure = 730 Torr, P_1 = 105 microns)

Fig. 4 – Effect of Orifice Displacement on Argon Beam Intensity
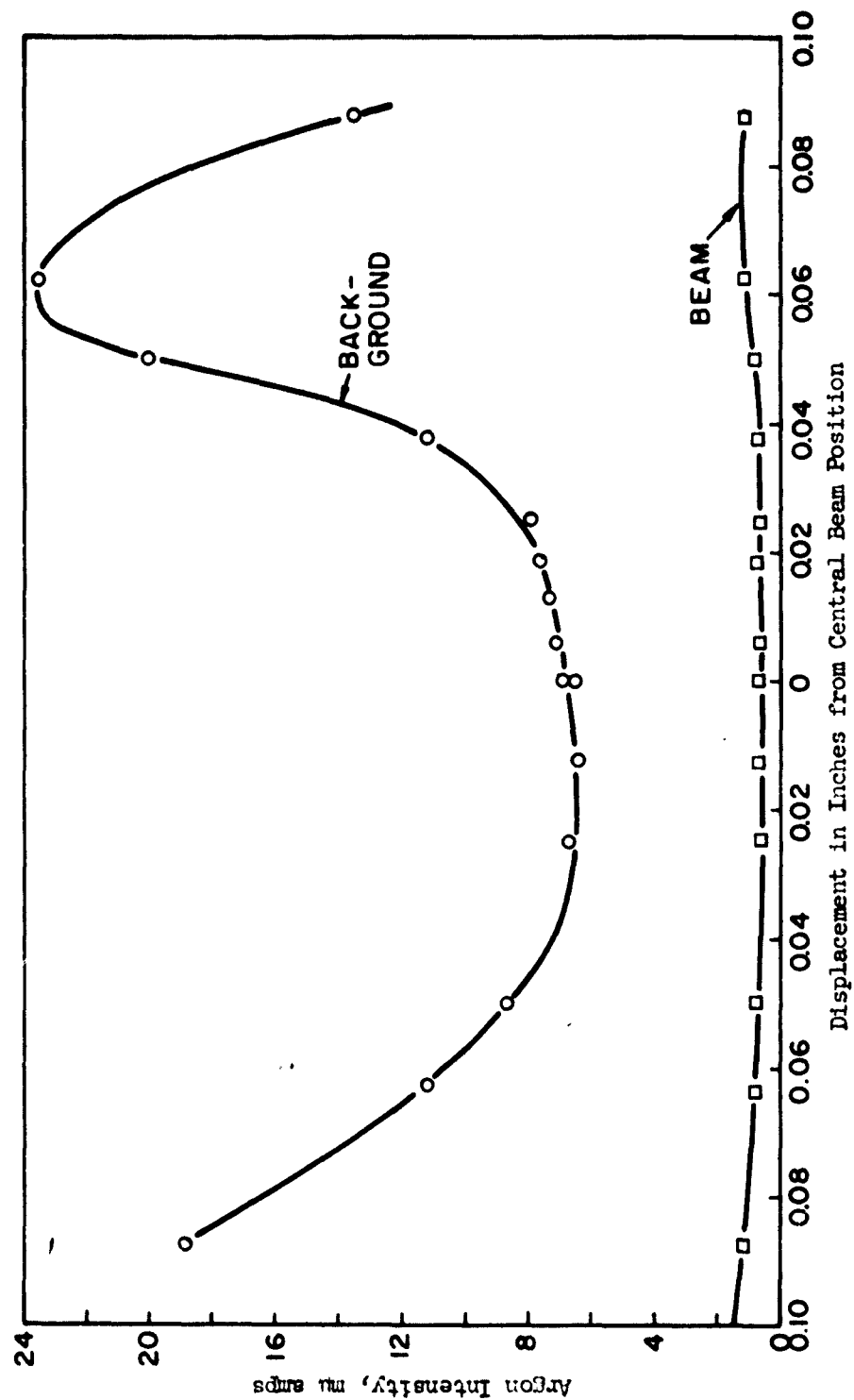(Orifice-to-Skimmer Distance = 13/32 in.,
Argon Pressure = 693 Torr)

Fig. 5 - Effect of Orifice Displacement on Argon Beam Intensity
(Orifice-to-Skimmer Distance = 17/32 in.,
Argon Pressure = 695 Torr)

B. Mixtures of Gases

The effect on a gaseous mixture of expansion to a supersonic jet has been studied, but the phenomena are not sufficiently well characterized to permit prediction for a given system. In general, the gas in the axis of the jet is enriched in the heavier component and this behavior has been rationalized theoretically on the basis of diffusion phenomena. Becker[1] reports separation factors, defined as the ratio of heavy/light molecules in the central stream to the same ratio in the peripheral gas, as high as 1.09 for Argon 40-36 and 4 for Ar/H_2. Likewise, Stern, et al.,[2] have studied mixtures in such jets, as have Chow and Masson.[3,4] Stern reports separation factors for Ar/N_2 as high as 1.30 and for Argon/He as high as 3.

These separation effects could be of importance in our high pressure sampling studies, since, in many cases, one may wish to know the relative concentrations of two species of different molecular weights to within the normal accuracy obtainable with mass spectroscopic detection. Consequently, we introduced a number of binary gaseous mixtures into the sampling system at various pressures and orifice-to-skimmer distances to assess the order of magnitude of such separation effects under our conditions.

In every case we found separation effects considerably larger than those previously reported. This may be due simply to the fact that with the direct conversion to a molecular beam, one is sampling gas contained in a very small solid angle along the axis of the original jet. As a matter of fact, we observed less pronounced mass separation effects in the background gas which comes in part from the much larger solid angle of total flow through the skimmer.

The separation of the mass 40 and mass 36 isotopes of Argon has been studied under a variety of conditions. This separation has been found to be remarkably insensitive to variation in source pressure (Fig. 6), orifice-to-skimmer distance (Fig. 7), and temperature. In the latter case, virtually the same mass separation was observed in a CH_4-O_2-Argon mixture both when the gases were unlit (T $\simeq$ 300°K) and when sampled from a burning flame (T $\simeq$ 2500°K). Figure 6 shows that the mass separation decreases only slightly from 700 to 25 Torr source pressure. The sharp apparent decrease in the background ratio is presumably due to the presence of a mass 36 background intensity from a source other than the Argon. Figure 7 indicates that for all settings at which a reasonable molecular beam is obtained, there is little variation of mass separation.
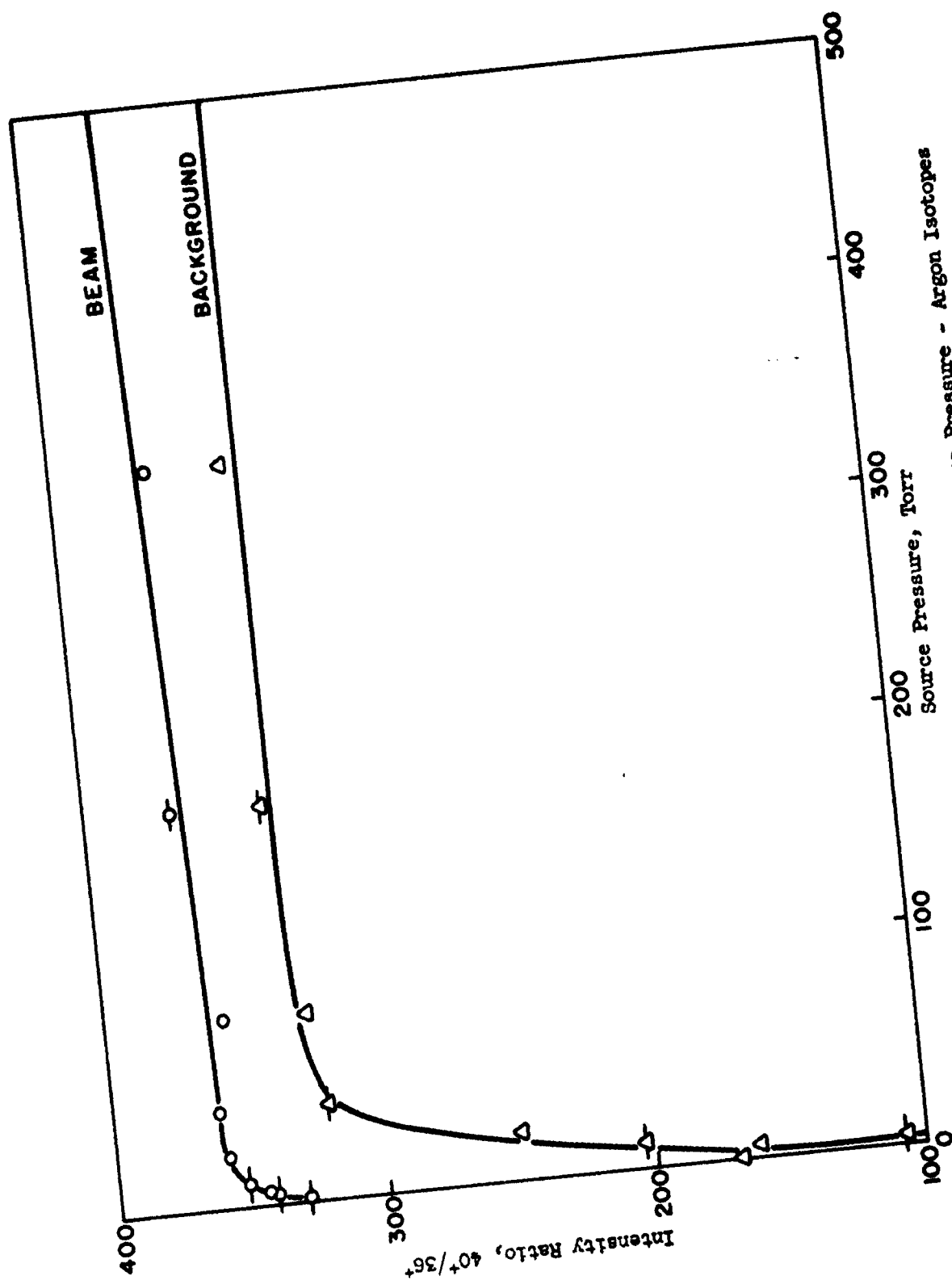
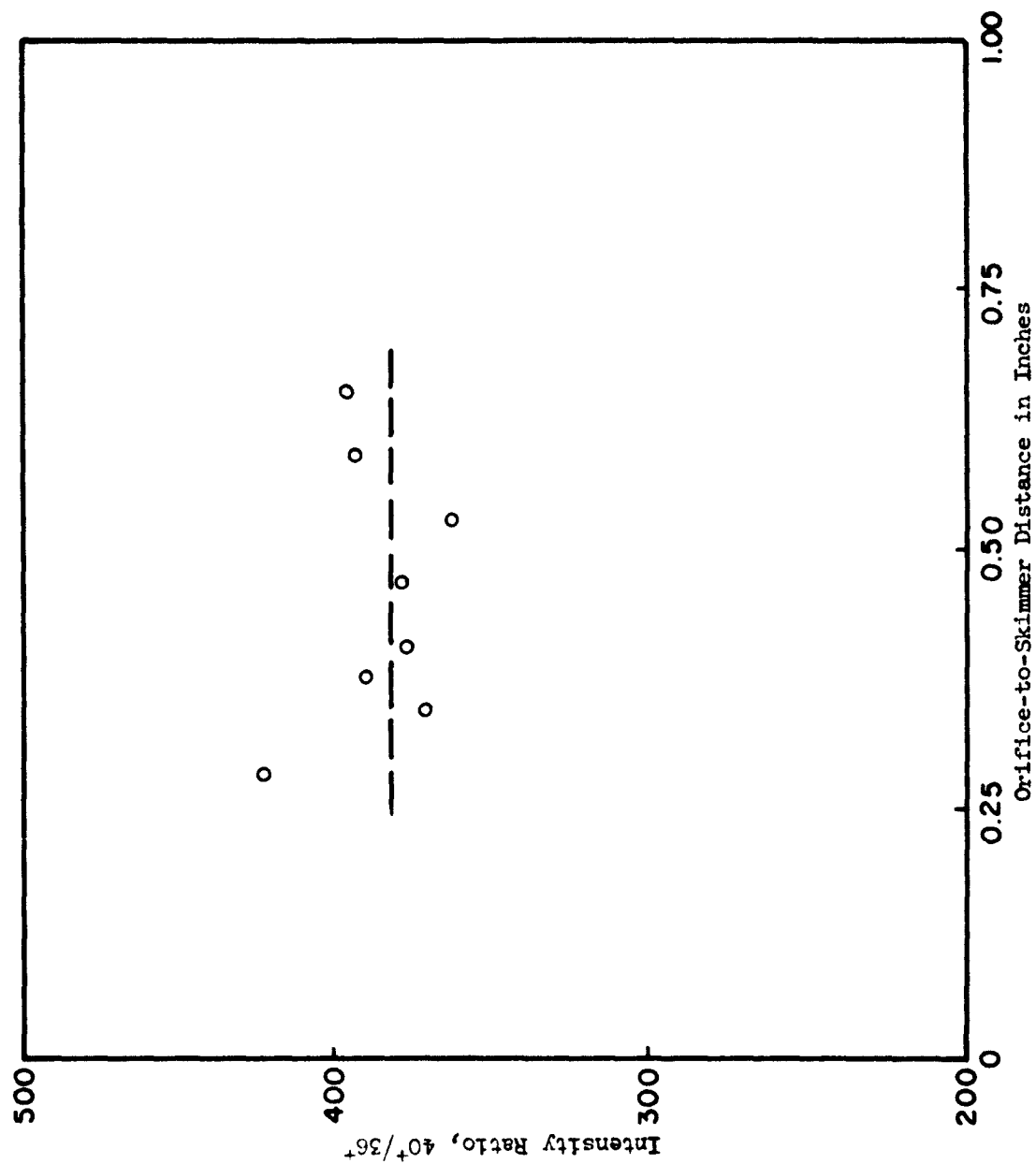Fig. 6 - Variation of Mass Separation With Source Pressure - Argon Isotopes

Fig. 7 - Variation of Mass Separation With Orifice-to-Skimmer Distance - Argon Isotopes at 1 atm.

Orifice-to-Skimmer Distance in Inches

Intensity Ratio, $40^+/36^+$

Mass separation effects in all the equimolar mixtures of Argon, N_2, CH_4, He and H_2 have been run in a preliminary survey, many at several pressures and orifice-to-skimmer distances. Also determined were the ion ratios when the same mixtures were leaked first into the ion source and then into stage 1, so that the skimmer acted as the gas source.

The actual beam and expansion conditions varied widely due to the different flow rates of mixtures through the same orifice. In addition, there is some ambiguity in comparing relative ion intensities as measured in the molecular beam and as leaked into the ion source directly, since the latter depend on the relative mass spectrometer pump-out rates for the different gases.

Results are shown for a H_2-Argon equimolar mixture as a function of orifice-to-skimmer spacing in Fig. 8 and as a function of misalignment of the bottom orifice in Figs. 9, 10 and 11. Results for CH_4-H_2 are shown in Fig. 12 as a function of source pressure. These results are typical of other mixtures although the effects are much more pronounced due to the large mass differences. In Table I are summarized the maximum separations observed for various combinations, together with the background ratio, the ion source and stage one leak ratios and the relative ionization cross sections of the two gases for the ions actually observed. In the last column is listed a measure of the enrichment of the heavier molecule in the beam.

About all that can be concluded from these preliminary data, taken under varying conditions, is that in every case there is an enrichment of the heavier mass component in the beam and that this enrichment varies roughly with the mass ratio of the two components. A more pertinent experiment, in terms of our flame studies, will be to add small amounts of a number of permanent gases of different molecular weights to the flame gases under the sampling conditions actually to be used. Stern has observed a mass separation between C_2H_4 and N_2 even though the molecular weights are the same. He found an enrichment of C_2H_4 in the central stream. Our first measurement with this mixture shows a much larger effect in the opposite direction. If mass separation effects can differ significantly for two gases of the same molecular weight, then there will be an inherent uncertainty in using calibrating-gas mass separation data for species like N_2O_4 and NO_2 or metal compounds in flames.
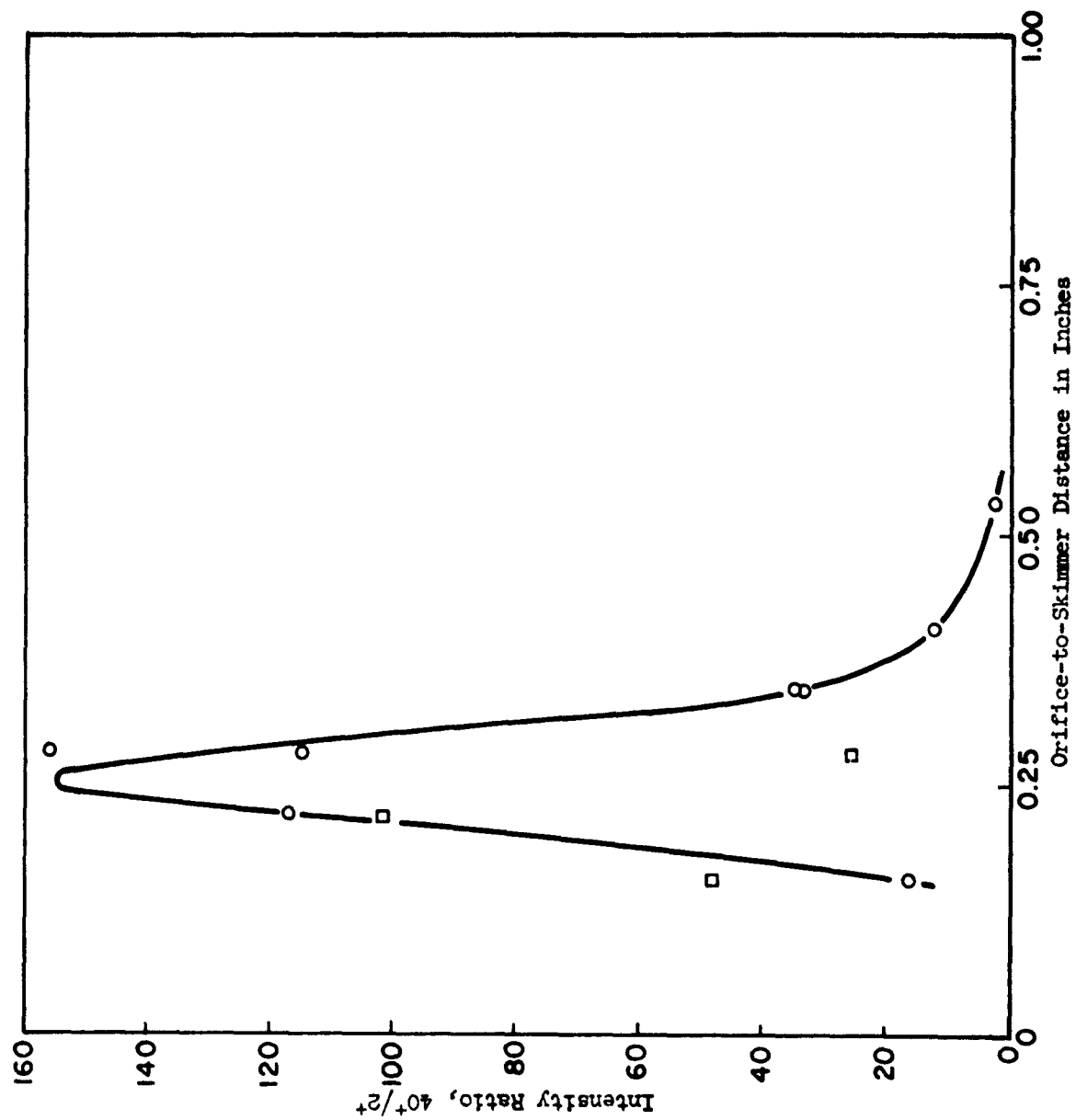
Fig. 8 - Variation of Mass Separation With Orifice-to-Skimmer Distance - H_2-Argon Equimolar Mixture at 1 atm.
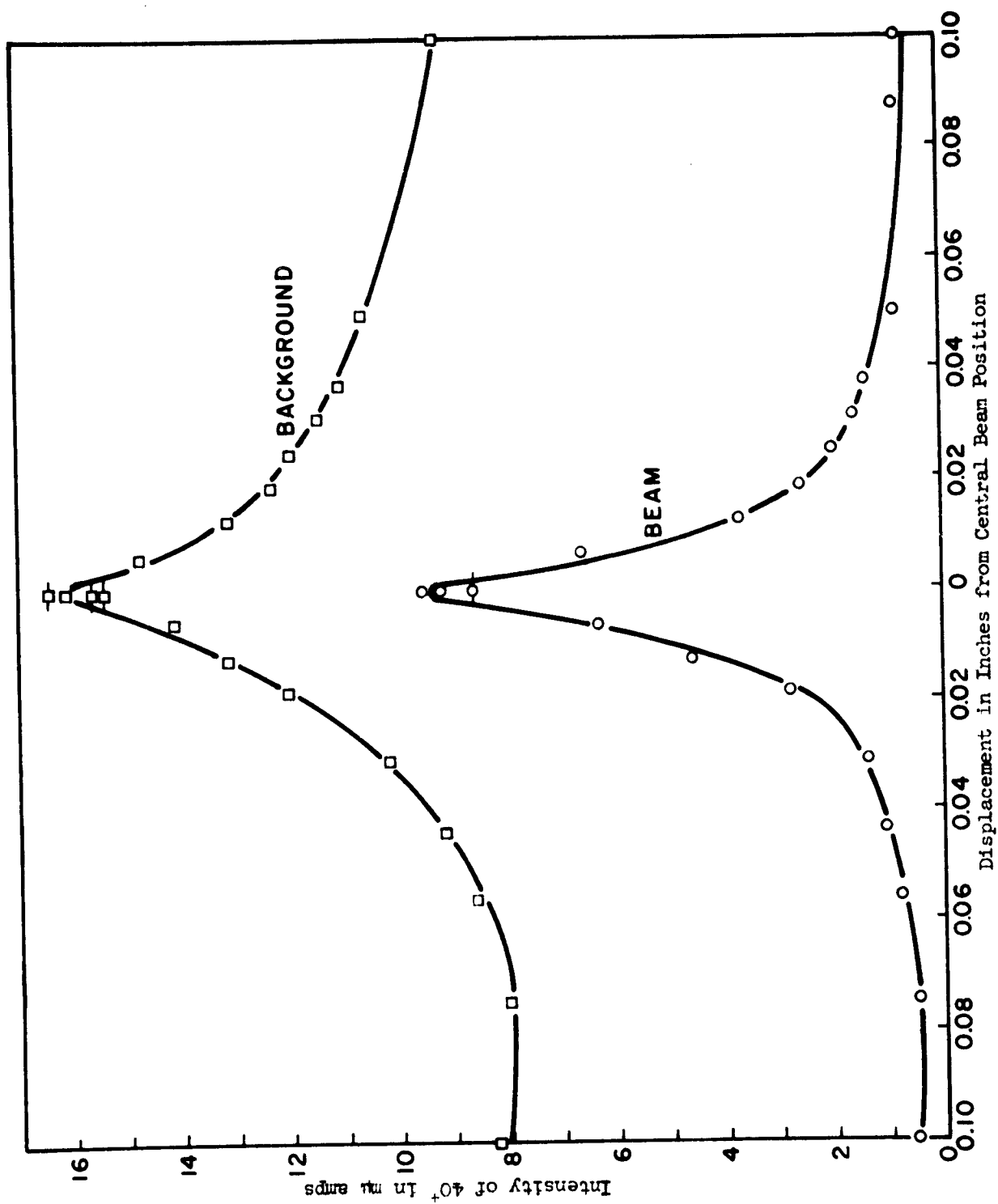
Fig. 9 - Variation in Argon Beam and Background With Orifice Misalignment -
H_2-Argon Equimolar Mixture
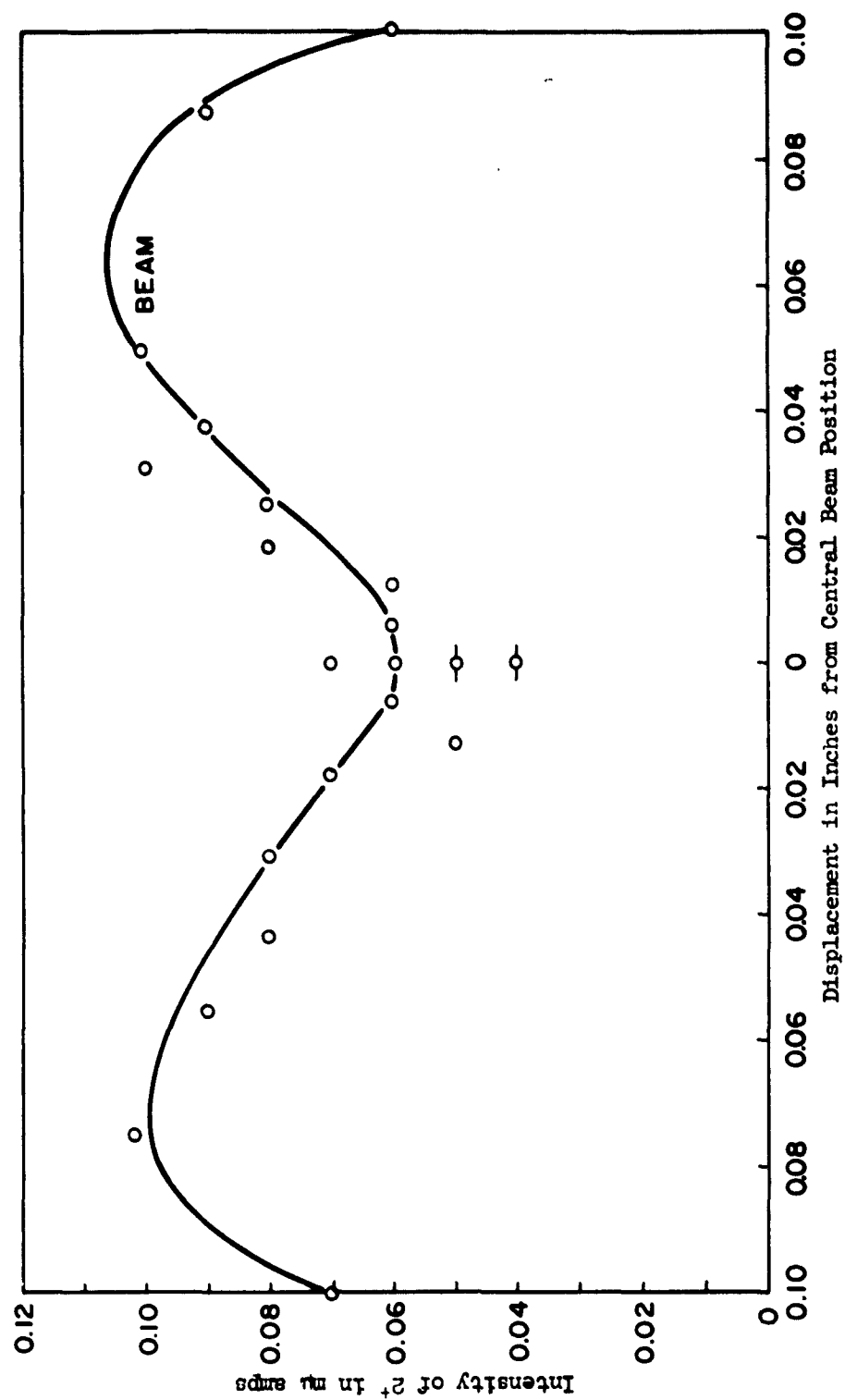
Fig. 10 - Variation in H_2 Beam With Orifice Misalignment -
H_2-Argon Equimolar Mixture
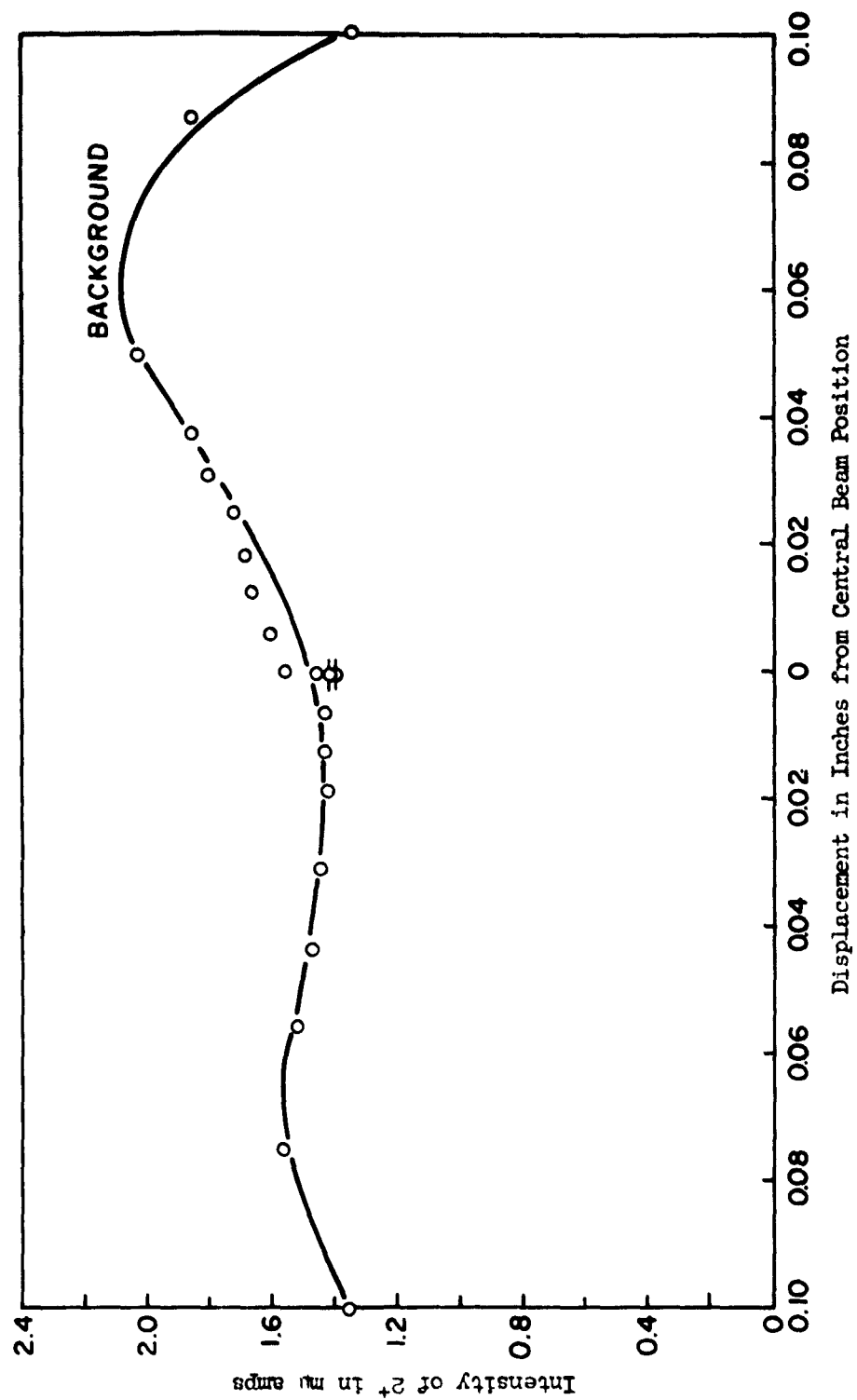
Fig. 11 - Variation in H_2 Background With Orifice Misalignment - H_2-Argon Equimolar Mixture
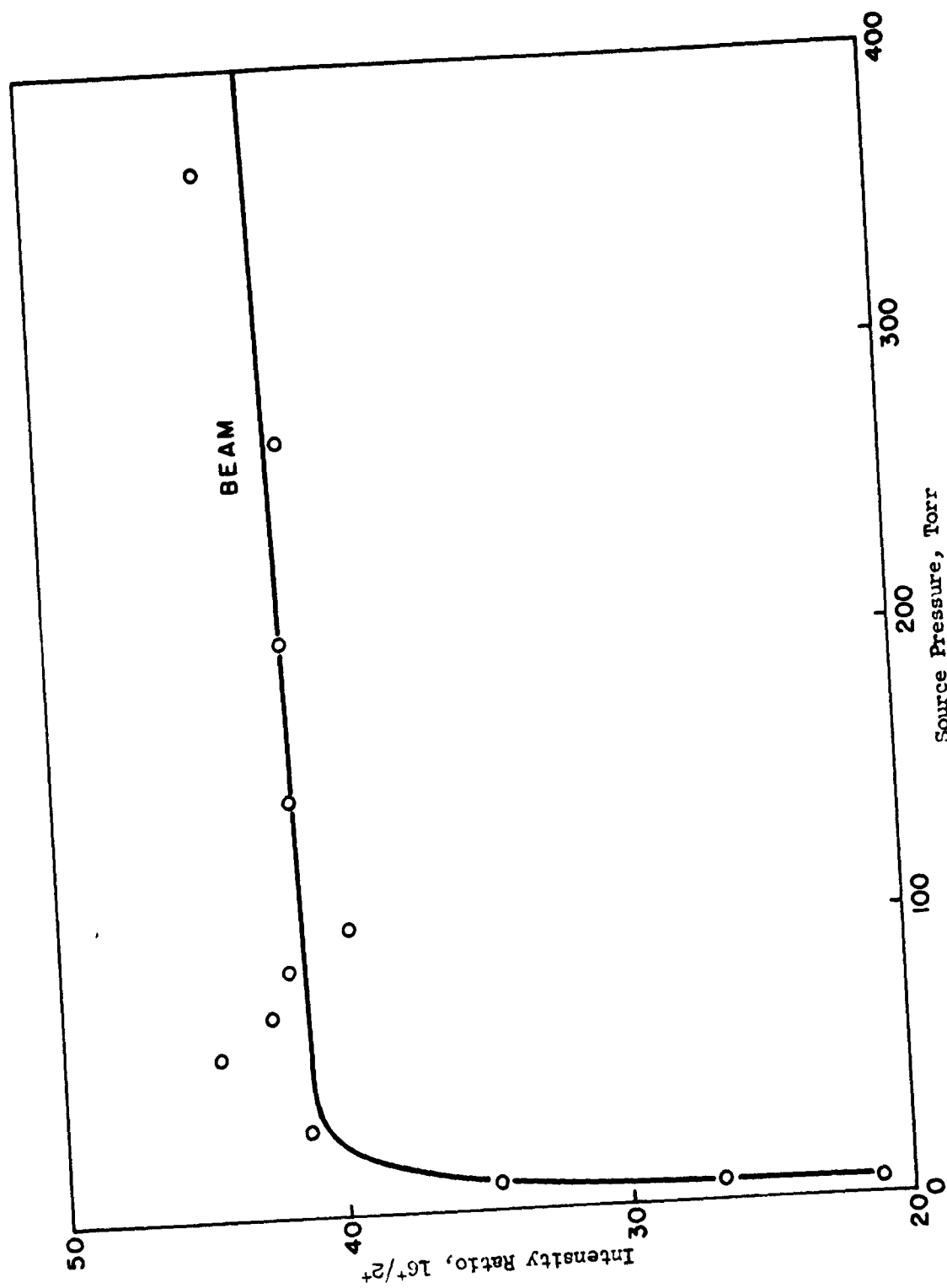
Fig. 12 - Variation of Mass Separation With Source Pressure in CH_4-H_2 System

TABLE I

MASS SEPARATION EFFECTS OBSERVED WITH
BINARY MIXTURES AT ONE ATMOSPHERE

Mixture (equimolar)	Mass Ratio	Beam	Background	Ion Source Leak	Stage 1 Leak	Calc. From Cross Section	Beam/ Ion Source Leak
N_2-C_2H_4	1.0	5.4	3.1	2.9	4.9	2.0	1.8
Ar40-36 (isotopic mixture)	1.11	370.0	320.0	310.0	260.0	300.0	1.2
N_2-O_2 (air)	1.14	0.27		0.21			1.3
Ar-N_2	1.43	2.9	1.4	1.3	1.2	1.2	2.3
N_2-CH_4	1.75	10.3	5.7	5.2	4.9	2.4	2.0
He-H_2	2.0	0.80	0.20	0.17	0.12	0.36	4.8
Ar-CH_4	2.5	16.0	2.6	2.10	1.8	2.8	7.6
N_2-He	7.0	93.0	46.0	26.0	28.0	9.9	3.6
CH_4-H_2	8.0	38.0	5.0	3.7	2.7	1.5	10.0
Ar-He	10.0	88.0	37.0	17.0	17.0	12.0	5.2
N_2-H_2	14.0	190.0	10.0	7.4	6.8	3.6	25.0
Ar-H_2	20.0	120.0	9.0	4.5	3.2	4.3	26.0

III. THE N_2O_4-NO_2 EQUILIBRIUM

The N_2O_4-NO_2 system is being studied since it provides a test of the ability to quench a highly reactive species, N_2O_4, in a system of known thermodynamics and kinetics at room temperature. In addition to the pressure sensitive NO_2^+/NO^+ ratio reported in the last quarterly report, we have carried out measurements on the $N_2O_4^+/NO_2^+$ ratio as a function of pressure. The $N_2O_4^+$ parent peak is very weak, apparently amounting to only a small fraction of the ions originating from N_2O_4, and hence it can only be measured quantitatively over a limited pressure range. The behavior of this ratio is shown in Fig. 13 for one of several runs which do not agree well with each other. Further data must still be taken to allow a reliable estimate of the fraction of the N_2O_4 quenched. However, major emphasis will now be shifted to flame studies with systems of known thermodynamics as described below.

IV. FLAME SAMPLING STUDIES

Our work so far has consisted of (1) a measurement of stable combustion products for a number of CH_4-O_2-Argon flames, (2) a search for free radicals in one atmosphere flames, and (3) the addition of a boron compound to a H_2-O_2 flame.

A. Stable Combustion Products

A simple test of quenching is to measure the stable reaction products of a series of flames of varying mixture strength and compare these with the expected equilibrium values. For a series of three CH_4-O_2-Argon mixtures representing a lean, stoichiometric and rich flame, the products H, H_2O, CO, O_2, Argon and CO_2 were measured as a function of burner-to-orifice distance. The burner was a small glass Meeker burner about 1/2 in. diameter. The first orifice was a flat, 0.005 in. thick, platinum disk with an 0.010 in. diameter hole.

The calculated flame temperatures, as kindly supplied by Mr. T. 0. Dobbins, varied from about 2270 to 2490°K. The partial pressures of species like H_2, CO, O_2 and CO_2 varied by factors of 2, 3, and more from flame to flame. Our sampling results agreed with the computed compositions within 10 - 15 per cent when one compared the changes in a given species such as H_2 or CO from one flame to another. The relative proportions of products in any one flame agreed less well. In fact, in every case H_2O^+ was quite low and H_2^+ even lower, consistent with the operation of mass separation effects of the order of magnitude listed in Table I. Individual species showed the expected behavior in the burnt gas region with definite evidence of entrainment of air at larger burner distances. More careful measurements of this type, together with flame temperature measurements, will be made on those flames to which metals will be added.
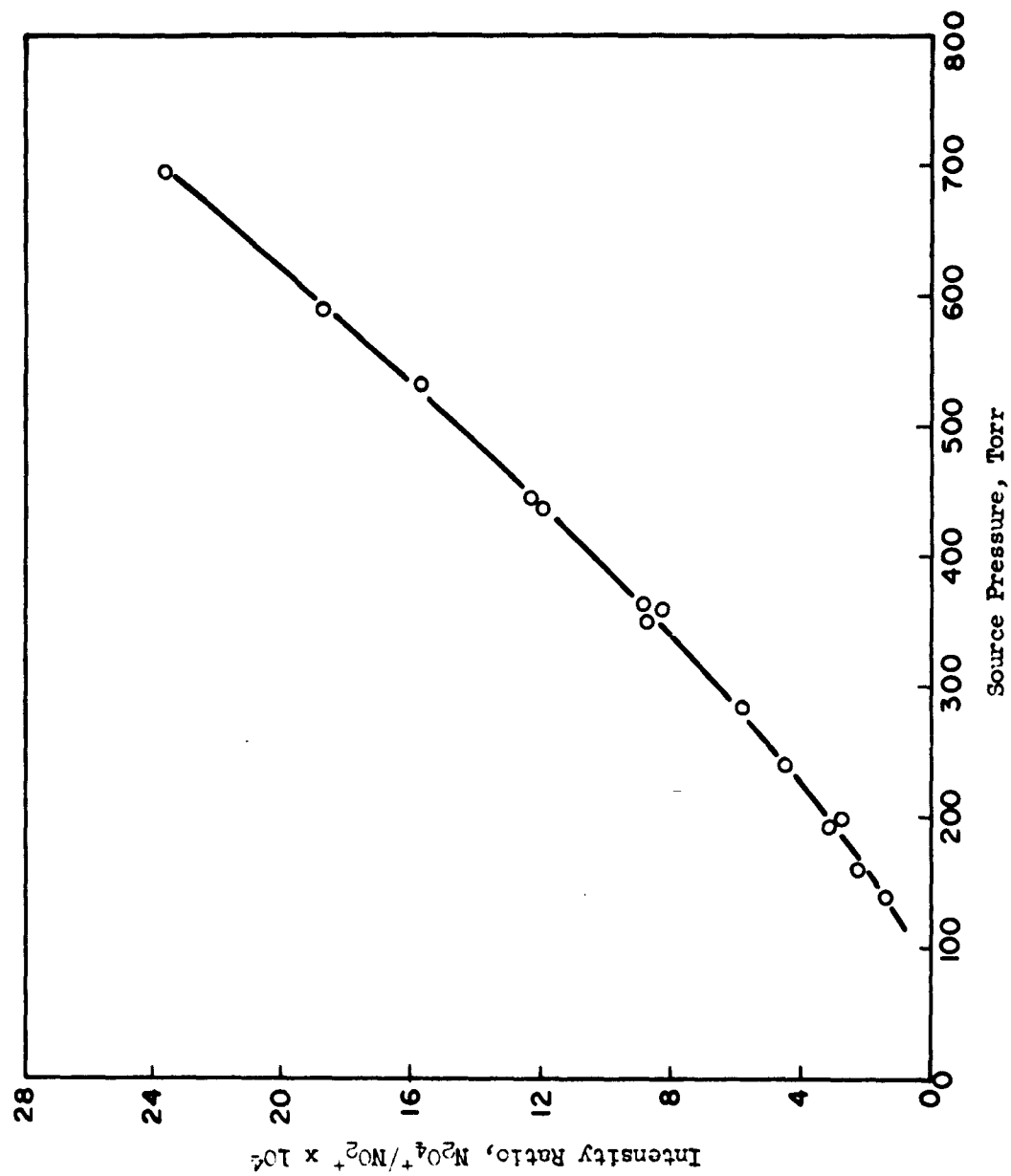
Fig. 13 - Variation of $N_2O_4^+/NO_2^+$ With Pressure

B. Free Radicals in Flames

The ability to quench the expected equilibrium amounts of the free radicals H, O, and OH from the burnt gas of flames should be the most severe test of our sampler. In fact, to our knowledge, no one has yet successfully sampled these free radicals from a one atmosphere flame. The mass spectrometric detection of such radicals is complicated by the always present fragmentation ions at the same mass from H_2O, H_2, CO, CO_2 and O_2. Thus, one must usually work at rather low ionization voltages to suppress the fragmentation contribution relative to the free radical parent ions.

We have searched for the OH and O radicals in CH_4-O_2-Argon flames under a variety of conditions but so far have no clear-cut evidence that they are reaching the ion source. It is expected that in view of the large mass separation effects observed it would be practically impossible to see H radicals even if they were not altered chemically during sampling. We will continue to search for such radicals, particularly with the hotter flames.

C. Metal Additives in Flames

We have added metals to premixed flames by means of water solutions of salts, using a de Vilbiss nebulizer, but so far not in concentrations high enough or in flames hot enough to detect the resultant species in the mass spectrometer. It is hoped that development of this technique will provide a general way of adding metals to flames at concentrations approaching 0.1 mole per cent.

Meanwhile, certain metals of interest are available as gaseous compounds which can be conveniently dispersed in the flame gases. As a first test of sampling reaction products of a metal in a flame, we have added BCl_3 to an H_2-O_2 stoichiometric flame. The theoretical temperature of this flame is about $3080°K$. This very high flame temperature required the use of a small flame. A standard O_2-H_2 torch was used with a tip diameter of only 0.023 in. The orifice, in the shape of a cone spun out of 0.005 in. platinum, was soft soldered to a water-cooled brass flange. With the flame raised very near this orifice, the central portion became white hot and, over the course of several hours, began sagging in with a gradual increase in orifice size. One orifice, initially 0.010 in. diameter, enlarged to 0.015 in. diameter after a day's use, but still produced satisfactory beams with the hot flame gases, although not with cold gases at one atmosphere. Future orifices will be made from Pt-Rh alloy in the hope of gaining mechanical strength. With the orifice cone this hot near the center there was little condensation of B_2O_3 except on the colder portions and plugging was gradual and perhaps took place as much on the cold skimmer as on the hot orifice.

In our preliminary experiments about 0.8 per cent BCl_3 was added to the stoichiometric H_2-O_2 flame, all gases being metered through flow meters. The mass spectrum was analyzed and shutter-dependent and BCl_3-dependent ion peaks were detected at masses 10, 11, 35, 36, 37, 38, 43 and 44. These peaks may be reasonably assigned to $(B^{10})^+$, $(B^{11})^+$, $(Cl^{35})^+$, $(HCl^{35})^+$, $(Cl^{37})^+$, $(HCl^{37})^+$, $(B^{11}O_2)^+$, $(HB^{10}O_2)^+$, and $(HB^{11}O_2)^+$. No other boron or chlorine containing species were observed.

The shutter-dependent intensities of the several observed ions are given in Table II.

TABLE II

IONS AND THEIR INTENSITIES OBSERVED WITH 0.8 PER CENT BCl_3
ADDED TO A STOICHIOMETRIC H_2-O_2 FLAME AT ONE ATMOSPHERE

Mass/Charge	Intensity (x 10^{12} amp.)
10	0.24
11	1.0
35	20.0
36	35.5
37	7.0
38	12.0
43	3.5
44	9.5

The intensities of masses 43 and 44 are probably low compared to the others, as the data were taken later and the sampling system was slowly plugging. The shutter dependencies for masses 10, 11, 35, 36 and 37 were virtually 100 per cent, in contrast to the stable species we have observed. Background at masses 38, 43 and 44 caused substantial signals even with the shutter closed.

The expected equilibrium composition of the flame was calculated assuming the theoretical flame temperature and composition given by Gaydon[5] for H_2-O_2 and assuming that the 0.8 per cent BCl_3 did not alter the H_2-O_2 species composition. Data for the various chlorine and boron species were taken from the JANAF tables.[6] Thermodynamic data for BO_2 were estimated.

The species considered were Cl, HCl, Cl_2, BCl, BO_2, BCl_3, BOCl, HBO_2, B_2O_3, BO_2, H_2BO_2, H_3BO_3, HBO, B_2O_2, and BO. All species were found to be

negligible except Cl, HCl and HBO_2. Consequently, taking into account the changing number of moles on combustion, the product percentages were computed to be: HBO_2 = 0.98 per cent, HCl = 2.16 per cent, and Cl = 0.79 per cent. The HCl-Cl equilibria should provide an interesting test of quenching ability. From the data in Table II and correcting for the fragmentation pattern of HCl determined in a separate experiment, one obtains an HCl^+/Cl^+ ratio of 2.47, within 10 per cent of the calculated value.

This agreement is certainly better than could be expected in view of uncertainties about the true flame temperature and composition. Perhaps the most significant result of this experiment is that we were able to quench significant quantities of the free radical Cl and the condensible molecule HBO_2 from the flame.

These encouraging results suggest further experiments with this system with careful attention to position in the flame of the sampling probe, measured flame temperatures, changes in flame composition and temperature and amount of BCl_3 added.

The interesting molecules BO, B_2O_2, BO_2 and B_2O_3 are all suppressed by the high water partial pressure in the H_2-O_2 flame. A nonhydrogen containing fuel will be required to study these species. About the only choice is the C_2N_2-N_2-O_2 flame system, with the N_2 or some other inert gas added to reduce the temperature of this exceedingly hot flame to manageable values. The CO-O_2 flame does not burn well without added H_2 but may be useful where trace amounts of H_2 do not interfere with the desired equilibria. In the cyanogen-O_2 system we should be able to look at the equilibria $1/2\ B_2O_3(g) + 1/4\ O_2(g) \rightleftharpoons BO_2(g)$ and $B_2O_2(g) \rightleftharpoons 2BO(g)$.

V. FUTURE WORK

Work will continue on the interesting problem of the characterization of the beam and the parameters which affect it, only to the extent that it appears to affect our ability to quench reactive species and to obtain intense beams. The mass separation problem, however, will require further investigation, primarily under the actual conditions of our flame studies, in order to assess the inherent uncertainty in measuring ratios of species with substantially different masses. This is particularly pertinent for third-law thermodynamic studies of species in the flame.

A few more experiments will be carried out in an attempt to straighten out the N_2O_4-NO_2 results and determine the degree of freezing of equilibria actually being achieved from one atmosphere.

Flame studies will be centered around additives to flames, such as BCl_3 where the thermochemistry is reasonably well known. The problem of actual temperature measurements in the flames will be pursued together with consideration of flame-orifice interactions, flame size and distance from the orifice, etc. The techniques of handling and measuring $C_2N_2-N_2-O_2$ flames will be developed since this flame should be particularly useful in investigating species in oxidizing atmospheres.

REFERENCES

1. Becker, E. W., et al., *Z. Naturforsch*, 10a, 565 (1957) and 12a 609 (1957).

2. Waterman, P. C., and Stern, S. A., *J. Chem. Phys.*, 31, 405 (1959) and 33, 805 (1960).

3. Chow, R. R., "On the Separation Phenomenon of Binary Gas Mixture in an Axisymmetric Jet," HE-150-175 Tech. Report, University of California, Institute of Engineering Research, Berkeley, California, November 1959.

4. Masson, B. S., "Diffusive Separation of a Gas Mixture Approaching a Sampling Probe," *ibid.*, Tech. Report HE-150-206, October 1962.

5. Gaydon and Wolfhard, "Flames, Their Structure, Radiation and Temperature," 2nd Edition, p. 301 (1960) Chapman and Hall, London.

6. JANAF Interim Thermochemical Tables. Vols. I and II. Dow Chemical Company, Midland, Michigan.